SYNTHESIS OF 2,2-DINITROPROPANOL. STUDIES ON CONTINUOUS PREPARATION

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A program was undertaken to investigate various methods of preparing the 2,2-dinitropropanol (I), with the ultimate objective of developing a process suitable for large scale production. With the exception of one synthetic route, which will be discussed later, the key step in the synthesis of I is the preparation of 1,1-dinitroethane (II) or its nitronate salt. The conversion of II to I is straightforward using the method of Henry[1] in which an aqueous suspension of the dinitroparaffin is treated with formaldehyde in the presence of a basic catalyst. In practice, it is usually more convenient to start with the nitronate salt of the dinitroparaffin and add one equivalent of acid to the solution:

$$CH_3C(NO_2)=NO_2Na + CH_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} CH_3C(NO_2)_2CH_2OH + Na^+$$

The product is isolated by extraction with a solvent followed by removal of the solvent in vacuo to leave I in the form of a waxy white solid. The material prepared in this manner is of satisfactory purity for use as an intermediate in most reactions without further purification. Analytically pure I can be prepared by repeated sublimation in vacuo; it is quite hygroscopic when pure and its melting point (92-94°) is extremely susceptible to depression by small amounts of impurities.

At the outset of this work, two routes to II were known which appeared sufficiently attractive for investigation as potential production processes.

OXIDATIVE-NITRATION REACTION

The most convenient method for preparing gem-dinitro compounds involves the reaction discovered by Kaplan and Shechter[2] in which treatment of the nitronate salt of a primary or secondary mononitroparaffin with silver nitrate and an inorganic nitrite in aqueous media gives the corresponding gem-dinitro compound and metallic silver:

$$RCH=NO_2^- + 2\,Ag^+ + NO_2^- \longrightarrow RCH(NO_2)_2 + 2\,Ag$$

$$R_2C=NO_2^- + 2\,Ag^+ + NO_2^- \longrightarrow R_2C(NO_2)_2 + 2\,Ag$$

The reaction, which has been termed an oxidative-nitration process, has been used to prepare a variety of primary, secondary, and functionally substituted dinitroparaffins. The silver produced in the reaction may be separated and converted to aqueous silver nitrate by treatment with concentrated nitric acid; after pH adjustment of the resulting solution to 5-6, it is ready for re-use.

The preparation of I by this procedure was initially carried out in these laboratories via the intermediate sodium 1-hydroxy-2-propanenitronate, which in turn was prepared by treatment of a suspension of nitroethane in aqueous formaldehyde with sodium hydroxide:

$$CH_3CH_2NO_2 + CH_2O + NaOH \longrightarrow CH_3\overset{\overset{NO_2Na}{\|}}{C}CH_2OH + H_2O$$

$$CH_3\overset{\overset{NO_2Na}{\|}}{C}CH_2OH + 2\ Ag^+ + NO_2^- \longrightarrow CH_3C(NO_2)_2CH_2OH + 2\ Ag + Na^+$$

Overall yields of 65-70% (corrected for the purity of commercial grade nitroethane) were obtained. Principal drawbacks to this procedure were side reactions which could be suppressed, but not eliminated, by careful control of reaction variables:

$$2\ CH_3CH_2NO_2 + 2\ CH_2O + NaOH \longrightarrow CH_3\overset{\overset{NO_2}{|}}{C}(CH_2OH)_2 + CH_3CH{=}NO_2Na + H_2O$$

$$2\ CH_2O + OH^- \longrightarrow HCOO^- + CH_3OH$$

$$CH_2O + 2\ Ag^+ + 3\ OH^- \longrightarrow HCOO^- + 2\ Ag + 2\ H_2O$$

$$CH_3CH{=}NO_2Na + 2\ Ag^+ + NO_2^- \longrightarrow CH_3CH(NO_2)_2 + 2\ Ag + Na^+$$

To circumvent these side reactions, a modified procedure was developed in which the oxidative-nitration was carried out before the methylolation step:

$$CH_3CH_2NO_2 + NaOH \longrightarrow \underset{\text{III}}{CH_3CH{=}NO_2Na} + H_2O \qquad (1)$$

$$\text{III} + 2\ Ag^+ + NO_2^- \longrightarrow \underset{\text{II}}{CH_3CH(NO_2)_2} + 2\ Ag + Na^+ \qquad (2)$$

$$\text{II} + NaOH \longrightarrow \underset{\text{IIa}}{CH_3\overset{\overset{NO_2}{|}}{C}{=}NO_2Na} + H_2O \qquad (3)$$

$$\text{IIa} + CH_2O + H^+ \longrightarrow \underset{\text{I}}{CH_3C(NO_2)_2CH_2OH} + Na^+ \qquad (4)$$

$$2\ Ag + 4\ HNO_3 \longrightarrow 3\ AgNO_3 + NO + 2\ H_2O \qquad (5)$$

Under the conditions described below, laboratory yields in reactions 1-4 were approximately 98, 90, 98, and 97% respectively. With a 95% extraction recovery of I from the aqueous layer, this gives an overall yield of 80% based on nitroethane. A typical analysis of material produced by this method is given in Table 1. Reaction 5 is essentially quantitative and losses in this step are primarily mechanical; silver losses will be discussed later in this section. Reaction 1 was carried out at 0-10° in most instances, although temperatures up to 20° could be used without noticeable change in results; at temperatures above ambient, side reactions leading to trimethylisoxazoles become appreciable.[3] Using a 5-10% excess of sodium hydroxide, added with vigorous agitation to the nitroethane-water suspension, the reaction was complete within 10 minutes after completion of addition of the base. At this point, sodium nitrite was added and the resulting solution (at 0-10°) was added rapidly to a vigorously stirred solution of the silver nitrate maintained at -5 to

0°. As reaction 2 proceeded, a solid (presumably an intermediate complex[2]) separated and the mixture became extremely thick, then progressively less viscous as metallic silver separated; the reaction is accompanied by an exotherm, and external cooling was applied as required to keep the temperature below 20°. When the exotherm was over, 50% sodium hydroxide was added over a 15-minute period at 15-20° to convert II to its water soluble sodium salt (reaction 3) and to precipitate excess silver ion as silver oxide. After filtration and water washing of the silver, the pH of the combined filtrates was reduced to 9-10 with acetic acid; a 10% excess of 37% formaldehyde was then added and the acidification was continued until a pH of 5.0-5.5 was reached (reaction 4). The aqueous solution, containing 7-9% of I was then extracted with ethylene chloride either batchwise or in a countercurrent column. Extraction efficiencies of 94-96% were attained. The ethylene chloride solution of I was then concentrated in vacuo to the desired strength prior to use as an intermediate in subsequent reactions. The metallic silver recovered from the oxidative-nitration step was converted to silver nitrate by slurrying in water and treatment with a slight excess of 67% nitric acid at 30-40°. The pH of the resulting solution was then adjusted to 5-6 with sodium hydroxide; some silver oxide was formed in this step, but did not interfere with use of the solution in a subsequent oxidative-nitration, since the oxide is also converted to silver in the reaction.

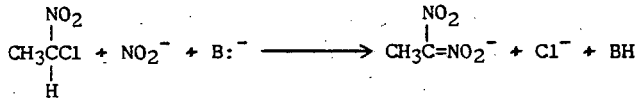
The procedure was adapted to batch pilot plant operation using 0.5 lb mole of nitroethane, and was eventually increased to a 2.0 lb mole scale. Although the overall yields on the pilot plant scale averaged about 5% lower than those obtained in laboratory preparations, the process presented no major scale-up problems. In initial pilot plant studies, silver was recovered by centrifuging the slurry after the neutralization step in which II was converted to its soluble sodium salt. In order to reduce silver losses due to handling, internal stainless steel filters were subsequently installed in the oxidative-nitration reactor and the slurry was pressure filtered rather than centrifuged. Using this procedure, the silver was not removed from the kettle from run to run; after filtration and washing, the silver was slurried with water and nitric acid was added to regenerate silver nitrate. Handling losses were reduced considerably and would have been reduced further had it not been for the occasional formation of very finely divided silver in the reaction. When this occurred, filtration was extremely slow and it was necessary to allow the slurry to settle, after which the supernatant liquid could be removed by siphoning. Subsequent washing of the silver was difficult and inefficient, and silver losses occurred despite filtration of the siphoned material. The cause of fine silver formation was not determined but appeared to be associated with the buildup of small quantities of organic material in the silver. Thus, once finely divided silver had formed, the problem was greatly magnified since it was difficult to wash the silver adequately, and the buildup of organic material in the silver cake increased rapidly in subsequent runs. It has been our experience that the best way to avoid this difficulty is to maintain a uniform dispersion of silver in the mixture by providing excellent agitation during the oxidative-nitration, neutralization, and silver washing steps.

Several hundred thousand pounds of I were produced by the oxidative-nitration method at this facility. Under normal operating conditions, silver losses averaged about 1%. Over short periods of time, losses ran as low as 0.5% and as high as 2%. The 1% loss can be tolerated for the preparation of development quantities of I but becomes a serious drawback for larger scale production. Other economic disadvantages to the process are the required use of expensive low-chloride grade sodium hydroxide (to avoid formation of silver chloride) and the relatively large quantities of nitric acid required to regenerate silver nitrate from recovered silver. A study of an alternate procedure, not requiring the use of silver nitrate, was therefore undertaken. It should be mentioned that a modification of the oxidative-nitration has been described recently[4] in which the reaction is carried out in an electrolytic cell, with silver ion being regenerated as it is consumed. While this procedure

shows promise of overcoming the problem of silver losses, a considerable amount of development work remains to be done before its ultimate potential for large scale production is known.

TER MEER REACTION

An alternate method for preparing salts of terminal gem-dinitro compounds that has been known for many years is the ter Meer reaction,[5] and involves treatment of 1-halo-1-nitroparaffins with nitrite ion in basic media to give the anion of the terminal gem-dinitro compound and chloride ion. In the case of 1-chloro-1-nitroethane the reaction is:



In practice it is desirable (by suitable choice of reaction solvent and/or metal cation) to force separation of the nitronate anion from the reaction mixture as a sparingly soluble salt as it is formed. In this manner, side reactions are suppressed and the reaction is driven to completion. Potassium ion is the cation of choice since potassium 1-nitro-1-ethanenitronate is sparingly soluble in water and essentially insoluble in most organic solvents; the sodium salt may be employed satisfactorily in nonaqueous systems but gives poor results in aqueous media, presumably due to its high solubility. The most commonly used solvents for the reaction are water, alcohol, or water-alcohol mixtures. The choice of base in the reaction is important. Strong bases, such as alkali metal hydroxides, give only fair results since they readily attack the 1-halo-1-nitroparaffin to give not only the nitronate salt but side reaction products resulting from cleavage of both C-NO_2 and C-Cl bonds. Extremely weak bases result in slow rates and incomplete reaction. Best results have been obtained using carbonates or, specifically, potassium carbonate. Reaction temperatures of 0-25° and times of 30-120 minutes are generally used; good agitation is essential to high conversions since the reaction system is heterogeneous regardless of the solvent employed. The product, potassium 1-nitro-1-ethanenitronate, is usually purified by filtration and washing with methanol to remove organic impurities which are adsorbed on the salt. This operation is undesirable inasmuch as the potassium salt, when dry, is quite sensitive to detonation by shock. It has a 50% fire point of less than 5 cm using a 2 kg weight in the Bureau of Mines impact tester (about the same as nitroglycerin). The material may be handled safely, provided it is kept wet with water or an organic solvent. The degree of improvement in impact stability depends upon the amount and nature of the solvent; water or aqueous alcohol is quite effective in amounts in excess of 30% based on the weight of the dry salt. The salt is easily converted to the dinitro-alcohol, I, by treatment with aqueous formaldehyde and acid as described in the previous section.

The ter Meer route to I was investigated at these facilities several years ago, both on a laboratory and small pilot plant scale. The best grade of 1-chloro-1-nitroethane available at the time in the quantities required was material of 80% purity. It also contained nitroethane (9.0%), 2-nitropropane (1.2%), 2-chloro-2-nitropropane (3.7%), and 1,1-dichloro-1-nitroethane (6.1%). In the laboratory, overall yields of I ranging from 57-62% (corrected for purity of the starting material) were obtained; the purity of I was acceptable (95-98%) provided the potassium salt of dinitroethane was filtered and washed thoroughly with methanol before proceeding with the methylolation reaction. However, procedures designed to avoid isolation of the hazardous salt on a pilot plant scale gave product of inferior quality. Thus, when the crude product slurry of the potassium salt was treated directly with formaldehyde and sulfuric acid, and the resulting product isolated by solvent extraction and vacuum stripping, product purity was only 85%;

the bulk of the impurities were those present in the original 1-chloro-1-nitroethane. When the aqueous product solution of I was extracted with n-hexane to remove impurities before the ethylene chloride extraction, an improvement in quality to a maximum of about 93% was obtained. In view of these results, and taking into account the cost of 1-chloro-1-nitroethane at the time ($1.50/lb, available in development quantities only), work on this route to I was discontinued in favor of the oxidative-nitration process. Recently, however, it was shown by other workers[6] that the method commonly used to prepare 1-chloro-1-nitroethane, namely, the reaction of aqueous sodium ethanenitronate with chlorine, gave a product of considerably improved purity

$$CH_3CH{=}NO_2Na + Cl_2 \longrightarrow CH_3\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}NO_2 + NaCl$$

under certain reaction conditions. These results were confirmed and led to a detailed study of the chlorination reaction, as well as to a re-examination of the ter Meer route to I. Emphasis was placed on the development of continuous processes; batch runs were used primarily to outline the most promising conditions for continuous operation.

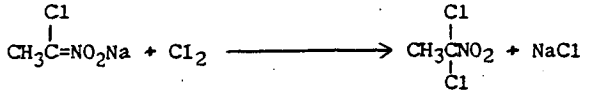
Preparation of 1-Chloro-1-Nitroethane. The first step in the synthesis, the conversion of the weak acid, nitroethane, to its sodium salt, presents little difficulty by either batch or continuous methods. Nitroethane is simply treated with aqueous sodium hydroxide at 0-10° in a well agitated vessel; in our work it was advantageous to employ concentrations which gave a solution containing approximately 23% of the salt. In batch runs, a sodium hydroxide addition time of 15 minutes and a post addition stirring period of 15 minutes gave excellent results. In continuous runs using the two stage reaction system shown in Fig. 1, a residence time of 45 minutes gave essentially complete conversion. Much shorter reaction times can be employed satisfactorily using extremely vigorous agitation, provided the heat of reaction (approximately 14 kcal/g mole) can be removed from the system. Aqueous sodium ethanenitronate is stable for a minimum of 24 hours at 0-10°; prolonged storage times and/or higher temperatures result in gradual degradation of the salt. The samples of commercial grade nitroethane used throughout these studies had a purity range of 92.8-93.3%; the balance was composed of nitromethane (0.5-1.5%), 2-nitropropane (4-6%) and traces of 1-nitropropane and nitrobutanes. It was found possible to effect a partial purification during sodium salt formation by using an amount of sodium hydroxide exactly equivalent to the nitroethane content of the commercial material. When this was done, a small amount of oil remained on top of the aqueous layer (pH 11.0) after the salt formation reaction was complete. Separation and chromatographic analysis of the oil showed it to contain 90.6% 2-nitropropane, 9.3% nitroethane, and 0.1% nitromethane. The reason for this selectivity of reaction with sodium hydroxide was not investigated but may be due to difference in solubility of 2-nitropropane and nitroethane in water (1.7 and 4.5 ml per 100 ml of water, respectively).

The conversion of the aqueous sodium salt to the chloro derivative was found to proceed extremely fast even at 0°; crude product separated from the reaction mixture as it was formed. The most important reactions occurring in the system are:

$$CH_3CH{=}NO_2Na + Cl_2 \longrightarrow CH_3\overset{\displaystyle Cl}{C}HNO_2 + NaCl \qquad (6)$$

$$CH_3\overset{\displaystyle Cl}{C}HNO_2 + NaOH \longrightarrow CH_3\overset{\displaystyle Cl}{C}{=}NO_2Na + NaCl \qquad (7)$$

$$CH_3CH{=}NO_2Na + CH_3\overset{\displaystyle Cl}{C}HNO_2 \longrightarrow CH_3CH_2NO_2 + CH_3\overset{\displaystyle Cl}{C}{=}NO_2Na \qquad (8)$$



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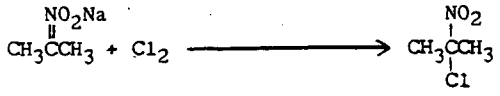

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Reactions 7, 8, and 9 lead to formation of the byproduct 1,1-dichloro-1-nitroethane. Reaction 7 can be all but eliminated by close pH control of the sodium ethanenitronate feed solution. Reaction 8 can be minimized in batch reactions by using a non-agitated system to reduce contact between the aqueous salt solution and the organic product solution and by removing the product as it is formed; in a continuous system a slight excess of chlorine can be employed. Little can be done to suppress reaction 9, but if conditions are chosen as described above to minimize 7 and 8, there is little sodium 1-chloro-1-ethanenitronate present to undergo chlorination. The extent to which 10 proceeds is dependent, of course, upon the amount of 2-nitropropane in the starting material and upon the efficiency of layer separation after salt formation, as already described.

Throughout this work, vapor chromatography was used to determine composition of the chlorination products. Using a 5-meter column packed with GE-SF-96 silicone on 35/80 Chromosorb, nitromethane, nitroethane, 2-nitropropane, and 1-chloro-1-nitroethane were separated quite satisfactorily; 1,1-dichloro-1-nitroethane and 2-chloro-2-nitropropane eluted at the same time under these conditions and were therefore recorded as a single value. Since the amount of 2-nitropropane in the starting material (nitroethane) remained almost constant, it was assumed that the amount of 2-chloro-2-nitropropane in the product remained constant at 1.5% and that any increase in the combined value for the chloronitropropane and the dichloronitroethane above 1.5% was due to formation of the latter material. Thus, a product giving combined value of 4.0% was assumed to contain 2.5% of the dichloro compound.

Initial chlorinations were carried out on a batch basis at 0-10° in a jacketed vessel equipped with a thermocouple well, fritted tube for chlorine inlet and a bottom takeoff for product removal. Although the initial pH of the salt solution was maintained at 11.0 and no agitation was used some dichloro compound was formed. The highest quality product obtained in this system contained 92.4% 1-chloro-1-nitroethane, 0.02% nitromethane, 1.6% nitroethane, 0.38% 2-nitropropane, and 5.60% 2-chloro-2-nitropropane plus 1,1-dichloro-1-nitroethane (4.1% of the latter based on the assumption above). Apparently, under these conditions there was enough contact between the organic and aqueous phase to permit reaction 8 to occur to some extent.

Most of the chlorination studies were conducted in continuous sytems. Coiled tube and straight tube reactors gave about the same results. A straight tube chlorination system is shown in Fig. 1a. Aqueous sodium ethanenitronate was metered by a proportioning pump to a pre-cooler maintained at -10 to -15°; the salt solution then entered the chlorination tube which was cooled by a brine system maintained at the desired temperature. Chlorine was fed directly to the tube through a rotameter. Effluent from the chlorinator passed to a decanter constructed to permit continuous overflow of spent aqueous layer at the top and product removal at the bottom. The pH of the spent aqueous layer was measured either directly in the decanter or in a line connected to the overflow system. When the pH of this layer was maintained at 5.5-6.5, essentially complete conversion was assured. Early in this work, no provision was made to measure the inside temperature of the chlorinator; it was assumed that it would be within 5-10° of the temperature of the circulating coolant. It was subsequently found that this was not the case and that temperatures in the reaction

zone were 30-90° higher than that of the coolant, depending on the system flow rates, chlorinator diameter, and coolant temperature. A typical profile of reaction zone temperatures as a function of residence time is shown in Fig. 2. The higher temperatures were not deleterious, provided the residence time at the higher temperature was kept to a minimum. Thus, as shown in Table 2, the purity of the chloronitroethane remained relatively constant (94.3-95.7%) over a wide range of flow rates and maximum temperatures in those cases where the residence time above 40° was less than one minute. As the time above 40° was increased to five minutes, product quality decreased rapidly to approximately 78%.

The necessity for maintaining the pH of the sodium ethanenitronate feed solution within a narrow range has been mentioned briefly. This was found to be the most critical variable in the system. As shown in Fig. 3, best results (i.e., high purity product and high conversions) were obtained in the pH range 11.0-11.15. Below this range, the conversion of nitroethane to its sodium salt is incomplete and low conversions to the chloronitroethane result. At higher pH ranges (11.3 and above) an excess of base is present, which results in conversion of 1-chloro-1-nitroethane to its sodium salt (reaction 7) and chlorination of the salt to give the dichloro compound (reaction 9). The experiments shown in Fig. 3 were carried out with slightly less (3-5%) than the theoretical amount of chlorine in the system. In subsequent work in which a slight excess of chlorine was used, total conversions above 95% and yields approaching 92% were obtained (Table 3).

Inasmuch as the chlorination reaction is quite exothermic (approximately 45 kcal/g mole), rapid heat removal in a production scale tubular reactor could not be accomplished without utilization of a complex and expensive system. This consideration led to evaluation of an agitated reaction system in order to provide rapid heat removal in a practical manner. It was feared that in an agitated system with intimate contact between organic and aqueous phases reaction 8 (salt interchange between reactant and product) would occur leading to formation of large amounts of the dichloro compound. However, when the system was investigated using a slight excess of chlorine at temperatures of 0-10°, product purity was at least as high as that produced in tubular reactors and yields were about the same. A comparison of results obtained in the two reaction systems is given in Table 3; a sketch of the agitated system is shown in Fig. 4. Apparently, the chlorination of sodium ethanenitronate proceeds at a much faster rate than salt interchange. To verify this qualitatively, a solution of 2.0 moles of 94.9% 1-chloro-1-nitroethane containing 0.17 mole of dissolved chlorine was stirred with 0.16 mole of aqueous sodium ethanenitronate for one hour at 0-10°. From the mixture, 2.13 moles of 94.8% 1-chloro-1-nitroethane were obtained, indicating the predominance of reaction 6 over 8. In a similar experiment in which the chlorine was omitted, 1.98 moles of 93.8% chloronitroethane were recovered which showed an increase of 1% in nitroethane content, indicating that reaction 8 does take place, but at a relatively slow rate.

Conversion of 1-Chloro-1-Nitroethane to 2,2-Dinitropropanol. The conversion of the chloro derivative to the alcohol was studied initially in batch runs to set conditions for a continuous process. In all work, the overall yield for the two step process was measured, since it was of interest to study the effect of variables during the ter Meer reaction on the final purity of the alcohol, as well as on yield. Conditions during the second step, the methylolation reaction, were kept constant from run to run. In batch runs, 1-chloro-1-nitroethane and an aqueous solution containing sodium nitrite and potassium carbonate were fed simultaneously to a jacketed vessel containing a heel of water; the temperature was maintained in the desired range by circulation of coolant through the jacket. It was shown early in this work that an addition time of one hour and a post addition stirring period of 30-60 minutes gave the best results in batch systems. These conditions were adopted as standard procedure for the evaluation of other variables.

It has been mentioned that isolation and solvent washing of the potassium salt of 1,1-dinitroethane, the product of the ter Meer reaction, was undesirable as a purification procedure due to the impact sensitivity of the dry material. A number of alternate purification methods were investigated, as shown in Table 4. The best method found involved addition of a sufficient quantity of water to completely dissolve the salt after completion of the ter Meer reaction and removal of organic impurities by extraction of the resulting solution with ethylene chloride. The extraction was then followed by the methylolation step. The yield and purity of I prepared by this method were almost identical to those obtained by the salt isolation procedure.

The effects of temperature and reactant ratios on yield were also investigated in batch runs. Temperatures of 15-20° gave best results, as shown in Fig. 5; at higher or lower temperatures, yields fell off slightly. A molar ratio of potassium carbonate/1-chloro-1-nitroethane of 1.0 gave best yields over the range studied (0.6 to 1.2), as shown in Fig. 6. An excess of nitrite ion favored high yields, as shown in Fig. 7; above a 20% excess, however, the increase in yield was slight. Thus, with molar ratios of sodium nitrite/1-chloro-1-nitroethane of 1.0, 1.2, and 1.6, overall yields of 63.7, 68.8, and 69.4% were obtained.

A continuous reaction system was constructed to operate under conditions indicated by the batch runs. The apparatus, shown in Fig. 7, was designed to carry out four steps on a continuous, integrated basis: 1) conversion of 1-chloro-1-nitroethane to the potassium salt of 1,1-dinitroethane; 2) dissolution of the salt in water; 3) extraction of the salt solution with ethylene chloride, and 4) conversion of the extracted salt solution to a solution of 2,2-dinitropropanol. The ter Meer reaction system consisted of three jacketed, cascade-type reactors connected in series so that the overflow was fed by gravity to the next reactor. Each vessel was stirred by a 2-1/4 in. diameter "Impellator" high shear stirrer at 870 rpm. The two feed streams, 1-chloro-1-nitroethane and an aqueous solution of sodium nitrite and potassium carbonate, were metered to the bottom of the first reactor (R-1) by proportioning pumps. Coolant was circulated through the reactor jackets to maintain the desired reaction temperature. The reaction product mixture overflowed the third reactor into a stirred dissolving vessel (V-1) to which water was metered to dissolve the potassium salt of dinitroethane; warm water was circulated through the jacket to maintain a temperature of 30-35°. The bottom outlet of V-1 was connected to a proportioning pump which metered this stream to the base of a modified Scheibel countercurrent extraction column. Another pump metered ethylene chloride to the top of the column to extract any unreacted 1-chloro-1-nitroethane and organic side reaction products. The column was operated so that the aqueous phase was continuous. The organic-free potassium salt solution overflowed the top of the extraction column and was mixed with a slight excess of 37% formaldehyde before entering the first stage of the methylolation reactor, V-2. This vessel was equipped with a jacket, stirrer, thermometer, bottom outlet, and a dropping funnel filled with 20% sulfuric acid. Coolant was circulated intermittently as needed to maintain a temperature of 25-30°. The delivery rate of the 20% sulfuric acid was adjusted to maintain the pH at 6.8-7.0. The combined streams left this vessel by gravity flow and passed to an open-top vessel equipped with a stirrer and a side outlet near the top. Additional sulfuric acid was added to maintain the pH at 4.0 to 4.5 in this vessel. The aqueous solution of I overflowed the side outlet and was collected for isolation of product by extraction with ethylene chloride.

A series of runs was made in this system in which reactant ratios were kept essentially constant, while temperature and residence time were varied. Results, shown in Fig. 8, closely paralleled those obtained in batch studies. In the temperature range 3-25° with residence times of 0.5-2.0 hours in the ter Meer reaction, the best yield (71%) was obtained at 17° with a residence time of 1.3 hours. Data from this run are shown in Table 5. Samples were collected over 2-hour periods

beginning at 4.5 hours after system start-up. Steady state was attained in about 8 hours as judged by leveling off of product yield. The system was run for a total of 24.5 hours and gave reasonably consistent results during the period 8.5-24.5 hours. The system operated smoothly and presented no foreseeable major obstacles from the standpoint of scale-up. A number of other runs, carried out for periods of 12-26 hours, also proceeded smoothly.

COMPARISON OF METHODS

Under the best conditions for both systems, the oxidative-nitration route to 2,2-dinitropropanol gives about a 15% higher overall yield (80% vs. 65% based on nitroethane) than does the ter Meer route. Chemical costs, however, for the ter Meer process are about one-half those for the oxidative-nitration process due to silver losses, the necessity of using an expensive grade of sodium hydroxide, and the use of large quantities of nitric acid to regenerate silver nitrate. Based on these considerations, and on cost estimates for manpower and facility requirements, it appears that the oxidative-nitration process is the superior method for preparing small or intermediate quantities of 2,2-dinitropropanol, whereas the ter Meer route becomes the more economical at higher production levels.

EXPERIMENTAL

Materials. Sodium hydroxide - U.S.P., maximum chloride content 0.005%. Nitroethane - commercial grade, used as received from Commercial Solvents Corp.; the various samples used in this work averaged 93% nitroethane as determined by vapor chromatography. Potassium carbonate - commercial grade, calcinated, 99.0%. Sodium nitrite - U.S.P., granular, 99.4%. Chlorine - commercial grade obtained from The Matheson Co., 99.5%. Silver nitrate - C.P. crystals, 99.98%. Formaldehyde - commercial grade 37% aqueous solution containing 7-8% methanol. Sulfuric acid - technical grade, 98%. Nitric acid - commercial grade, 67%. Acetic acid - glacial, 99.5%. Ethylene chloride - technical grade. Methanol - commercial grade. Potassium hydroxide - technical grade, 85%. Ethyl ether - analytical reagent grade.

Analysis of nitroethane and 1-chloro-1-nitroethane. Analysis by vapor chromatography was investigated using a number of columns under several sets of conditions. Best results were obtained using a Perkin-Elmer Model 154-D Vapor Fractometer equipped with a 0.1 mv Leeds and Northrup recorder and a Perkin-Elmer Model 194 integrator. The instrument was operated at 90° with 5 meters of column packed with GE-SF-96 silicone on 35/80 Chromosorb (Wilkins Instrument and Research Co., Walnut Creek, California). A helium flow rate of 45 cc/min at 10 psig was maintained using 5 micro-liters of sample. Each major (>0.01%) component was trapped by repeatedly running samples of the crude material through the fractometer until enough material was obtained for infrared examination and for recycle to the column at a known concentration. In this manner, nitromethane (peak 3, V_r° 496.8), nitroethane (peak 4, V_r° 715.2), 2-nitropropane (peak 5, V_r° 876.5), 1-chloro-1-nitroethane (peak 6, V_r° 1235.4), 1,1-dichloro-1-nitroethane (peak 7, V_r° 1498.8), and 2-chloro-2-nitropropane (peak 7, V_r° 1498.8) were measured. The latter two components eluted at the same time and were calculated as a single value. Peaks 1 and 2 were present to the extent of <0.01% and were not identified.

Analysis of 2,2-dinitropropanol. A 10-g sample was weighed into a tared Erlenmeyer flask and dissolved in 50 ml of anhydrous methanol. The solution was maintained at -5 to 0°C while 50 ml of a solution containing 6.5 g of 85% potassium hydroxide in methanol was added gradually with stirring. After addition, the thick yellow slurry of potassium 1-nitro-1-ethanenitronate was stirred for an additional 2-3 minutes at -5 to 0°. The mixture was suction filtered on a sintered funnel and washed 3 times with cold anhydrous ethyl ether. When dry, the potassium salt is extremely shock sensitive (impact sensitivity of less than 5 cm using a 2-kg

weight in the Bureau of Mines apparatus) and should be kept damp with solvent during handling operations. After the last ether wash, the salt was transferred (behind a safety shield) to a tared Petri dish and spread as thin as possible. The dish was placed on a balance and solvent allowed to evaporate until constant weight was reached. The sample was safely disposed of by quenching with water before removal from the balance.

Preparation of 2,2-dinitropropanol by the oxidative-nitration method. A suspension of nitroethane (150 g, 93% purity, 1.86 moles) and water (400 ml) was stirred vigorously while a solution of 50% sodium hydroxide (168 g, 2.1 moles) was added over a 25-min period while keeping the temperature at 0-10°. After addition was complete, sodium nitrite (144 g, 2.1 moles) was added and the mixture was stirred an additional 5-10 min. The mixture was added, over a 2-min period, to a vigorously agitated solution of silver nitrate (644 g, 3.8 moles) in 2400 ml of water which had been precooled to 0°. Two minutes after addition, the temperature had risen to 12° and the pH was 5.0. After stirring an additional 30 min at 10-15°, the mixture was treated with 50% sodium hydroxide, added over a 25-min period at 10-20°, until a pH of 12-13 was reached. The mixture was filtered and the silver washed three times with 400-ml portions of water. The pH of the combined filtrates was adjusted to 8.5-9.5 with acetic acid, and 37% formaldehyde (170 g, 2.1 moles) was added all at once. The pH was then adjusted to 5.0 with acetic acid at 20-25° over a 30-min period. After stirring an additional 30 minutes, the solution was extracted eight times with 400-ml portions of ethylene chloride. Removal of the solvent *in vacuo* left 230 g of 97% 2,2-dinitropropanol; overall yield, 79.9% based on the nitroethane content of the starting material.

Conversion of recovered silver to silver nitrate. Recovered silver (454 g) was slurried with 350 ml of water in a reaction vessel equipped with a caustic scrubbing system to remove oxides of nitrogen. With good stirring, 67% nitric acid (640 g) was added over a 4-hr period at 30-40°. Stirring was continued after addition for 1 hr at 40° and the pH of the solution was then adjusted to 5.0-5.5 by gradual addition of 50% sodium hydroxide.

Preparation of sodium ethanenitronate for chlorination studies. (a) Batch procedure. To a precooled and vigorously stirred mixture of 92.6% commercial nitroethane (900 g, 11.08 moles) and 1800 ml of water, 35.85% sodium hydroxide (1275 g, 11.11 moles) was added at 5-10° in 15 min. The mixture was stirred an additional 15 min, diluted to 4 liters, and transferred to a separatory funnel where the unreacted organic layer (the majority being 2-nitropropane) was separated. The lower aqueous layer was stored at 5° prior to use. The final solution contained 23.45% sodium ethanenitronate and had a pH of 10.6-11.0. (b) Continuous procedure. Continuous reactions were carried out in a two stage cascade reaction system (Fig. 1) equipped with paddle agitators and jackets through which coolant was circulated. Equimolar streams of 15% sodium hydroxide and nitroethane were fed to the first 400-ml reactor by proportioning pumps. The stage heights were arranged to permit gravity overflow from the first stage to the bottom of a second identical reactor. The product overflowing the second reactor was fed to a decanter for separation of unreacted 2-nitropropane from the aqueous product solution.

Conversion of sodium ethanenitronate to 1-chloro-1-nitroethane. (a) Tube chlorinator. A sketch of the tube chlorination system is shown in Fig. 1a; the reactor was a jacketed tube 1 cm I.D. x 72 cm long and was equipped with a thermocouple well which extended the length of the tube. Precooled aqueous sodium ethanenitronate and chlorine were fed to the tube inlet through a proportioning pump and a rotameter, respectively. Coolant, at the desired temperature, was circulated through the tube jacket. Effluent from the tube flowed to a decanter where the pH of the spent aqueous layer was measured. (b) Stirred chlorinator. The stirred chlorination system is shown in Fig. 4. The reactor (2.54 cm I.D. x

28 cm height) was equipped with a jacket for coolant circulation, thermocouple well, and paddle stirrer. Precooled aqueous sodium ethanenitronate was fed to the top of the reactor by a proportioning pump; chlorine was fed to a bottom inlet through a rotameter. The product mixture flowed by gravity to a decanter where the spent aqueous and organic layers were separated continuously. The pH of the aqueous layer was measured in the decanter. After separation of the crude product, it was dried with sodium sulfate (3 g per 100 g of crude product) and filtered before analysis. Yields were based on the amount of dried, filtered material recovered. When an excess of chlorine was used, a stream of air was blown through the crude material to remove dissolved chlorine before the drying step.

Batch conversion of 1-chloro-1-nitroethane to 2,2-dinitropropanol. Typical run. A solution of potassium carbonate (138 g, 1.0 mole) and sodium nitrite (82.8 g, 1.2 mole) in 500 ml of water was added simultaneously with 95% 1-chloro-1-nitroethane (109.5 g, 0.95 mole) over a 1-hr period to a vigorously stirred 100 ml heel of water at 12-18°. After the addition, the slurry of precipitated yellow potassium salt of 1,1-dinitroethane was stirred 30 min at 12-18°. The salt was dissolved at 25° by addition of 1400-1700 ml of water, and the resulting solution extracted twice with 300-ml portions of ethylene chloride. The aqueous layer was treated with 37% formaldehyde (60.4 g, 0.745 mole) and the solution acidified, over a 30-min period, to pH 4.0-4.5 with 400-500 g of 20% sulfuric acid. The solution was allowed to stir another 30 min and was then extracted with 12 aliquots of 150 ml of ethylene chloride. The combined organic extracts were stripped in vacuo to leave 100.6 g of 99.0% 2,2-dinitropropanol; overall yield, 69.9% based on the 1-chloro-1-nitroethane content of the starting material.

Continuous conversion of 1-chloro-1-nitroethane to 2,2-dinitropropanol. The apparatus employed in these studies is shown in Fig. 8. 1-Chloro-1-nitroethane (94-96% purity) and aqueous feed (1.2 moles of sodium nitrite and 1.0 mole of potassium carbonate per 600 ml of water) were metered separately to the first stage reactor of the ter Meer reaction system by proportioning pumps. Rates were adjusted to maintain a molar feed ratio of $CH_3CHClNO_2/NaNO_2/K_2CO_3$=0.95/1.2/1.0 and a total residence time of 0.5-2.0 hr in the three stage reaction system. The "Impellator" stirrers in each reactor were adjusted to a rate of 870 rpm. Temperature was controlled in the desired range by circulation of coolant through the reactor jackets; maximum temperature spread through the three stages was 3°. The potassium salt product slurry overflowed the third stage to a dissolving vessel to which water (2000 ml/mole of 1-chloro-1-nitroethane fed) was pumped; temperature was maintained at 30-35° by circulation of water through the jacket. The resulting potassium salt solution was pumped to the base of a modified Scheibel column. Ethylene chloride (1000 ml/hr in all runs) was pumped to the top of the column. The extracted aqueous effluent from the column was allowed to flow by gravity to a jacketed reaction vessel to which 37% formaldehyde (0.85 mole/mole of 1-chloro-1-nitroethane fed) and 20% sulfuric acid were added; pH in this reactor was maintained at 7.0-7.5 and the temperature at 25-30°. Effluent from this reactor was allowed to flow to a second vessel in which the pH was maintained at 4.0-4.5 by further addition of 20% sulfuric acid. Effluent from this reactor, containing about 3% 2,2-dinitropropanol, was collected as product. A complete weight balance was conducted for each sample. Aliquots (4 liters) of each sample were extracted twelve times with 300-ml portions of ethylene chloride; solvent was then removed in vacuo in a rotary evaporator with final heating of the residue at 45°/0.1 mm for 1 hr. Phase distribution studies showed that the extraction procedure described above gave a 96% recovery of product from the aqueous layer. Continuous extractions in the modified Scheibel column gave a 94% average recovery.

TABLE 1

TYPICAL ANALYSIS OF 2,2-DINITROPROPANOL PREPARED VIA THE OXIDATIVE-NITRATION REACTION

2,2-Dinitropropanol	97.0
Mononitro Compounds*	2.0
1,1-Dinitroethane	0.5
Formaldehyde	0.1
Silver	0.05
Water	0.1
Acetone Insolubles	0.1

*Includes nitroethane, 2-nitro-1-propanol and 2-nitro-2-methyl-1,3-propanediol

TABLE 2

EFFECT OF RESIDENCE TIME ABOVE 40°C ON THE PURITY OF 1-CHLORO-1-NITROETHANE

Run No.	Residence Time in Chlorinator, min.		Maximum Temp., °C	Mole % in Product	
	Total	Above 40°C		1-Chloro-1-Nitroethane	2-Chloro-2-Nitropropane 1,1-Dichloro-1-Nitroethane
1	1.35	0.31	68	95.7	1.50
2	1.72	0.30	58	94.8	2.34
3	3.70	0.52	58	95.6	1.86
4	4.88	0.00	39	95.7	1.87
5	6.90	0.73	50	95.5	2.50
6	10.40	0.55	50	94.3	2.39
7	17.50	1.23	50	92.5	3.70
8	9.90	5.57	76	78.5	8.65[a]
9	5.22	5.22	70	77.3	10.90[b]

[a]Also contained 11.9% nitroethane. [b]Also contained 10.6% nitroethane.

TABLE 3

RESULTS IN TUBE AND STIRRED CHLORINATORS

Run	pH of Sodium Ethanenitronate Feed	Residence Time, min. Total	Residence Time, min. Above 40°C	Type Reactor	% Yield	Product Analysis, Mole % Nitromethane	Nitroethane	2-Nitropropane	1-Chloro-1-Nitroethane	1,1-Dichloro-1 Nitroethane + 2-Chloro-2-Nitropropane
1	11.0	3.70	0.520	Straight Tube	84.0[1]	.130	1.16	1.07	95.62	1.86
1	10.7	6.90	0.740	"	87.0	.070	1.30	0.46	95.63	2.44
2	10.8	1.13	0.395	"	90.7	.075	1.65	1.25	95.06	1.97
3	11.0	9.45	0[2]	Stirred	91.6	.28	2.15	0.54	95.22	1.72
4	11.1	9.7	0[2]	"	90.5	.23	0.86	1.09	95.81	1.74
5	11.0	17.8	0[2]	"	89.5	.09	0.94	1.00	95.54	2.30
6	10.9	40.6	0[2]	"	87.3	.06	1.57	0.77	95.51	2.04

[1]pH of aqueous effluent maintained at 7.4-7.7; in all other runs the pH was maintained at 5.5-6.5. [2]Temperature maintained at 0-10°.

TABLE 4

PURIFICATION PROCEDURES FOR 2,2-DINITROPROPANOL PREPARED BY THE TER MEER REACTION

Run		2,2-Dinitropropanol % Yield	% Purity
1	Potassium salt of 1,1-dinitroethane filtered and washed with methanol before methylolation step.	69.4	99.2
2	Aqueous 2,2-dinitropropanol product solution extracted with n-hexane before isolation of product by ethylene chloride extraction.	67.7	93.4
3	Same as Run 2 except for substitution of cyclohexane for n-hexane.	71.3	95.8
4	Same as Run 2 except for substitution of toluene for n-hexane.	63.7	98.2
5	Dissolved potassium salt of 1,1-dinitroethane in water and extracted with methylene chloride before methylolation step.	58.3	98.0
6	Same as Run 5 except for substitution of ethylene chloride for methylene chloride.	68.8	99.6

TABLE 5

DATA ON CONTINUOUS CONVERSION OF 1-CHLORO-1-NITROETHANE TO 2,2-DINITROPROPANOL

Run & Sample	Sample Period, Hr.	Molar Feed Ratio $CH_3CHClNO_2/NaNO_2/K_2CO_3$	Ter Meer Residence Time, Hr.	Ter Meer Reaction Temperature, °C R-1	R-2	R-3	Total wt. Balance,%	$CH_3C(NO_2)_2CH_2OH$ Assay, %	Yield %
15-A*	4.5-6.5	0.938/1.2/1.0	1.30	17.0	15.0	14.3	100.9	98.7	68.4
15-B*	6.5-8.5	0.938/1.2/1.0	1.305	17.0	15.0	14.3	99.8	98.5	68.5
15-C	8.5-10.5	0.953/1.2/1,0	1.305	17.2	15.1	14.6	94.8	99.4	70.8
15-D	10.5-12.5	0.960/1.2/1.0	1.31	17.1	15.1	14.5	101.2	98.2	69.7
15-E	12.5-14.5	0.968/1.2/1.0	1.305	17.1	15.1	14.5	95.3	98.8	70.0
15-F	14.5-16.5	0.953/1.2/1.0	1.30	17.1	15.1	14.5	98.4	99.2	69.4
15-G	16.5-18.5	0.938/1.2/1.0	1.295	17.0	15.0	14.6	99.0	98.8	71.6
15-H	18.5-20.5	0.930/1.2/1.0	1.30	17.0	15.0	14.6	99.4	99.3	74.0
15-I	20.5-22.5	0.938/1.2/1.0	1.305	17.0	15.0	14.6	99.4	98.8	72.8
15-J	22.5-24.5	0.938/1.2/1.0	1.31	17.0	15.0	14.6	96.3	99.1	69.9
Average							98.4	98.9	71.0

* Not steady state (not included in average).

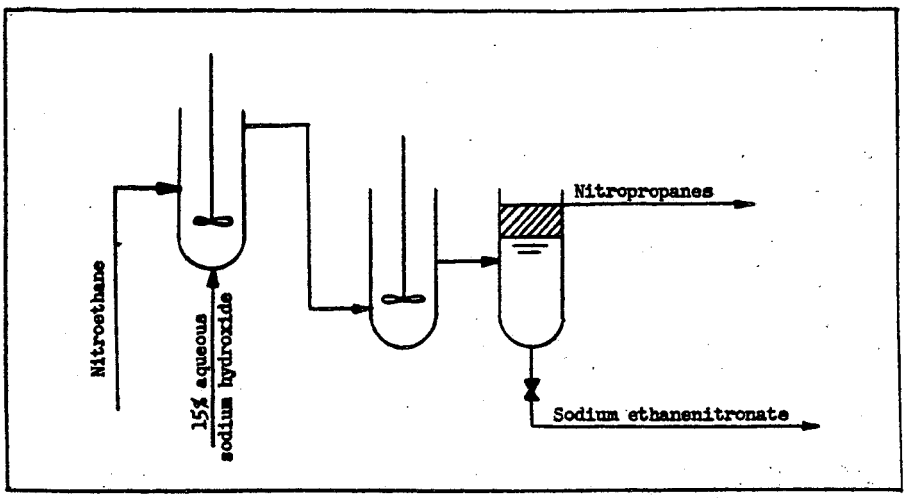

Figure 1. Reaction system for the continuous preparation of sodium ethanenitronate from nitroethane.

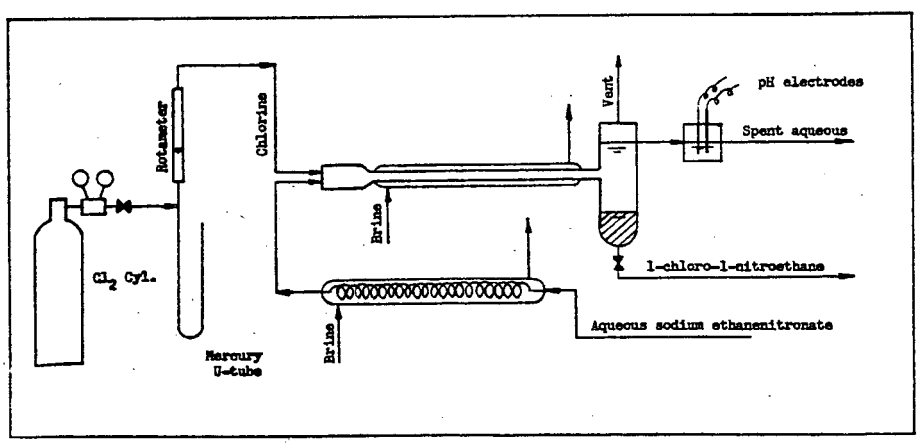

Figure 1a. Straight tube reactor system for the continuous conversion of sodium ethanenitronate to 1-chloro-1-nitroethane.

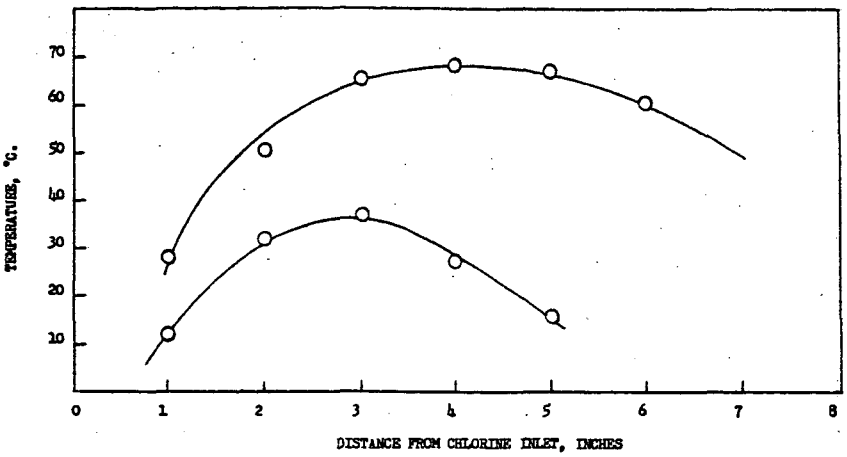

Figure 2. Reaction temperature profiles in straight tube chlorinator. Reactor length 28.4 inches. Sodium ethanenitronate concentration 2.76 m/l. Total residence time: A = 4.05 min., B = 1.35 min.

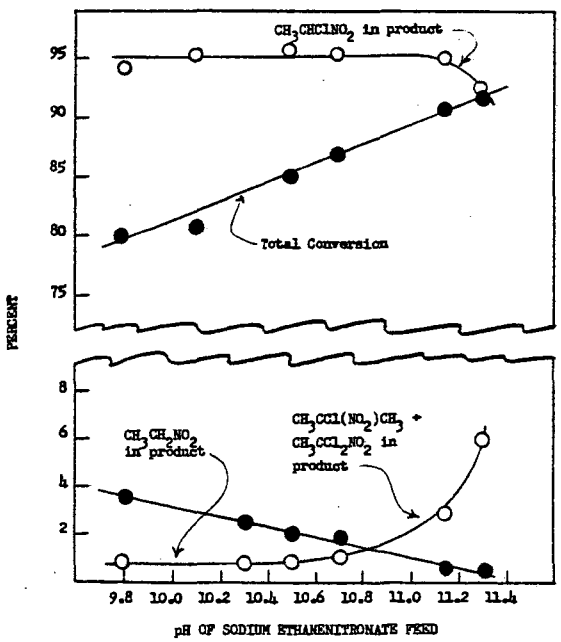

Figure 3. Effect of pH on conversion and product purity in continuous coiled tube reactor. Residence time 7 minutes.

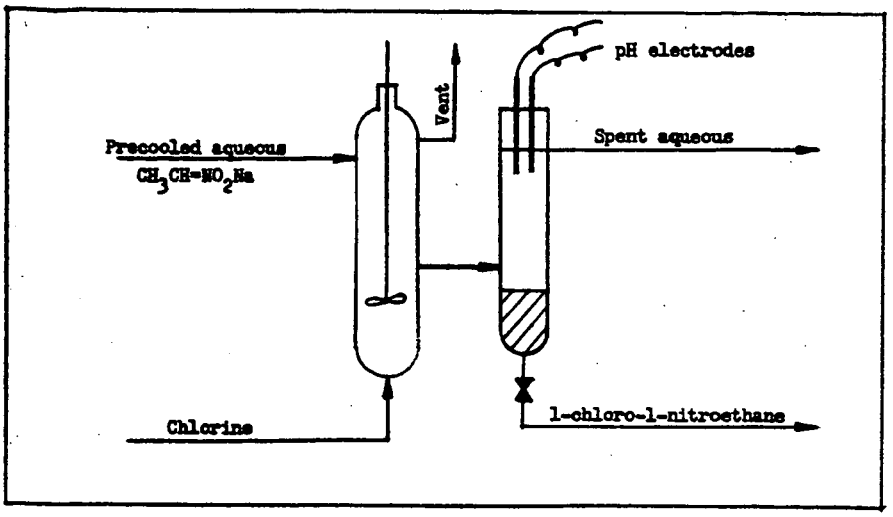

Figure 4. Agitated reaction system for the chlorination of sodium ethanenitronate.

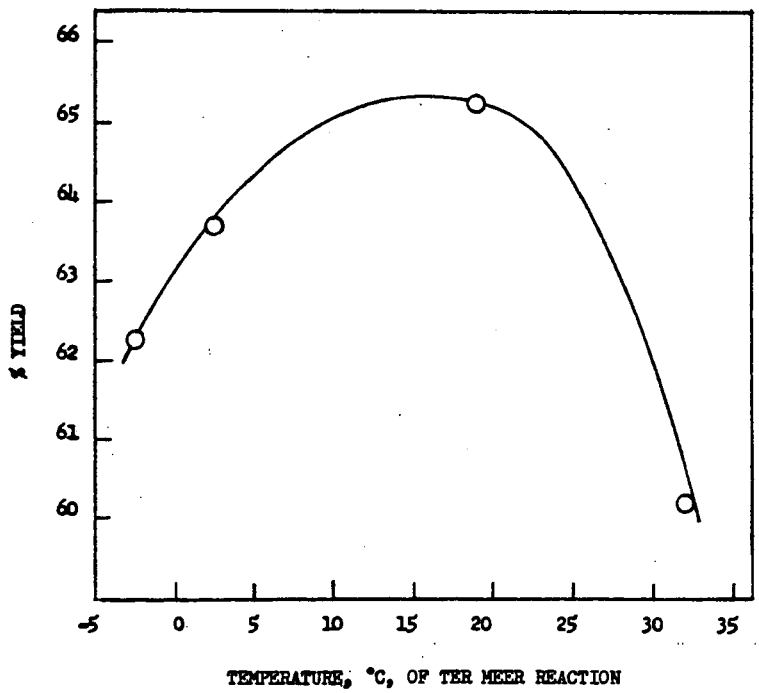

Figure 5. Effect of temperature during ter Meer reaction on 2,2-dinitropropanol yield in batch reactor. $NaNO_2/K_2CO_3/CH_3CHClNO_2$ molar ratio = 1.0/1.0/1.0.

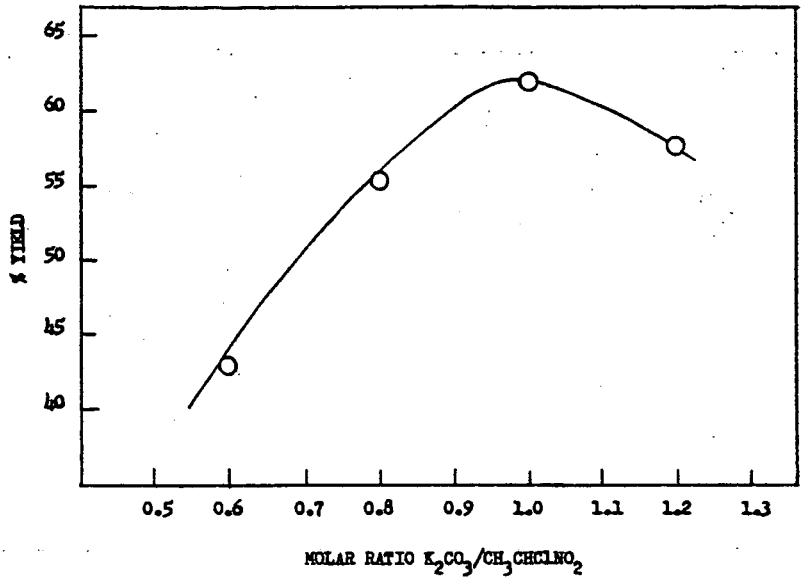

Figure 6. Effect of reactant ratios on 2,2-dinitropropanol yield in ter Meer reaction at 0 - 10°C in batch reactor. Molar ratio $NaNO_2/CH_3CHClNO_2$ = 1.0.

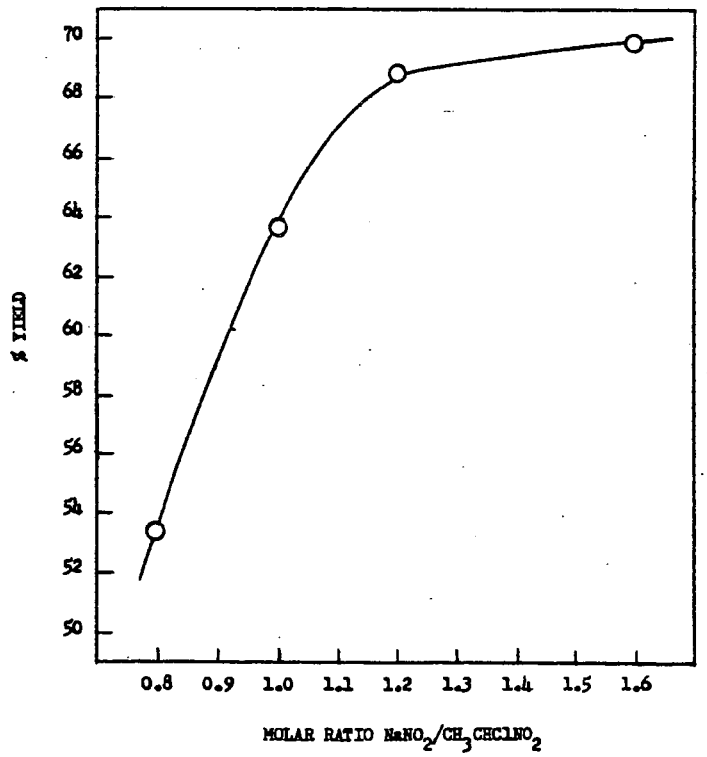

Figure 7. Effect of reactant ratios on 2,2-dinitropropanol yield in ter Meer reaction at 0 - 10°C in batch reactor. Molar ratio $K_2CO_3/CH_3CHClNO_2$ = 1.0.

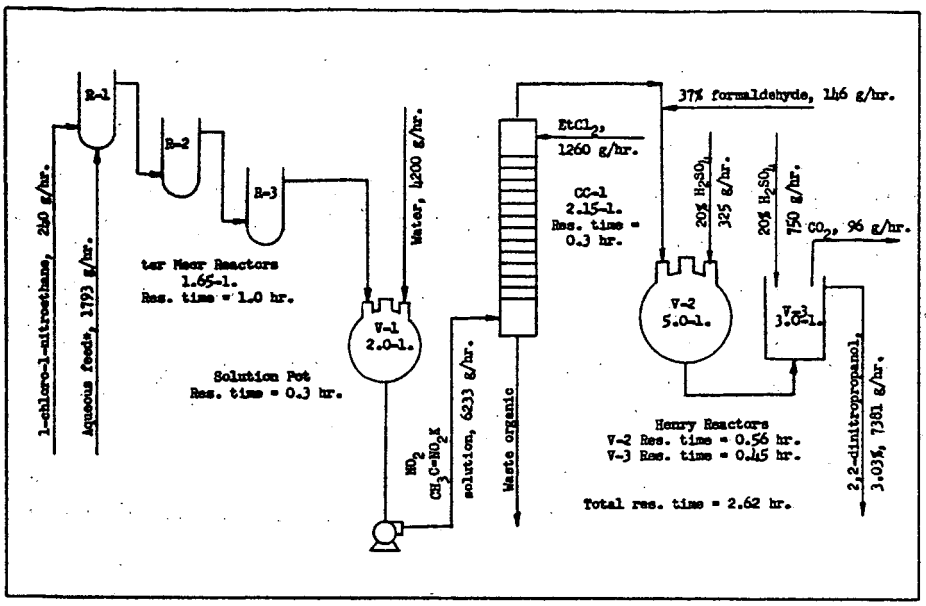

Figure 8. Reaction system for continuous preparation of 2,2-dinitropropanol from 1-chloro-1-nitroethane. *Aqueous feed was prepared by dissolving 83 g. $NaNO_2$ (1.2 mol.) and 138 g. K_2CO_3 (1.0 mol.) per 600ml. water.

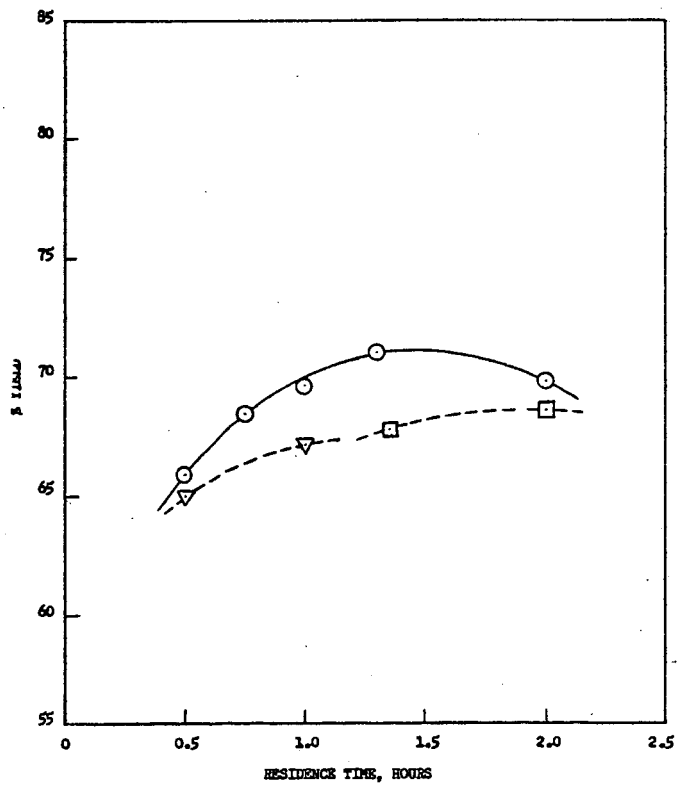

Figure 9. Effect of residence time on the yield of 2,2-dinitropropanol from 1-chloro-1-nitroethane via the ter Meer Reaction. Reaction temperature: ⊡ = 3°C, ⊙ = 17°C, and ▽ = 25°C.

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A Method for Studying Precombustion Reactions of Liquid Propellants

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Introduction

Since their inception, rocket engine development programs have been plagued with sporadic explosions. Some of these have occurred on start, others during a run, and still others on shutdown. Ordinarily, design changes are relied upon to correct such situations. A more fundamental approach was considered at Bell which consisted of looking at the chemistry of the system.

All work done along this line was based on the hypothesis that liquid phase reactions occur between rocket propellants and exert an influence on subsequent combustion reactions. In the case of nitric acid-hydrocarbon engines, e.g., liquid phase oxidation and/or nitration reactions appear possible. Depending on which reaction occurs or predominates, one can anticipate smooth or troublesome combustion.

Testing this hypothesis began with a literature survey which yielded little conclusive evidence. This led to a step-by-step experimental approach to rocket operating conditions of temperature, pressure and reaction time, and produced a useful method for studying precombustion reactions of liquid propellants.

Summary

The heart of the method was an apparatus designed to bring propellants separately to conditions of temperature and pressure equivalent to those encountered on injection into an operating rocket engine. The propellants were next flowed into the arms of a "Y"Tube, allowed to react in the stem, then subjected to a chemical stop. Reaction time was controlled by flow-rate and stem dimensions. In its final form this apparatus brought together propellants preheated to 300°F at 575 psig, allowed them to react for 15 milliseconds, and delivered the products in solutions suitable for conventional analyses. These analyses, largely spectrophotometric, showed to what extent particular reactions had occurred. Reaction mechanism was elucidated by analyses of products from parallel mixing experiments carried out under less drastic conditions and allowed to go to completion. The following is an account of the evolution of this apparatus and its role in the overall method.

Technical Approach

Experimental work began by mixing small quantities of typical propellants, WFNA (White Fuming Nitric Acid) and JP-4, in various proportions in the hope that at certain mixture ratios solutions would form which could be analyzed for oxidation products or explosives. Since little direction was afforded by the literature, initial mixing was done in open beakers without impressed heating. Exothermic reactions took place without incident in every case but no solutions resulted. Mixture ratio variation was achieved by dropwise addition of JP-4 in increments up to 15g. to 15g. of WFNA and vice versa.

To preserve all reaction products for analysis, the experiments were repeated using a two-neck flask fitted with a reflux condenser and thermometer. The set-up was contained in a water bath sitting on a magnetic stirrer capable of mixing the water and propellants. In these experiments heating was continued until reaction had ceased as evidenced by the cessation of nitrogen dioxide evolution. Temperature-time profiles were taken and the resulting mixtures were set aside for observation and analyses. Some showed a distinct third liquid phase assumed to be a collection of reaction products or the beginnings of solution formation.

At this point, mixing conditions were made more drastic in the hope of forcing solution formation. A three-neck flask was adopted and a high speed stirrer (1400 rpm) introduced. The flask was stationed on a hot plate. By this time analytical work had shown that the most interesting results were occurring at mixture ratios of O/F = 0.3, 1.0, 2.0, 4.0 and 5.0 so all future work was centered about these values. The procedure was much as before except that mixing time was varied within definite limits maintained by transferring the flask to an ice bath at the appropriate time. An extension of this work involved a series of high speed mixing studies carried out under the influence of intense light and/or sound. For these experiments the mixing flask was mounted in a box fitted with a lens which directed ultraviolet radiation of rocket engine intensity on the propellants. This reaction was from a filtered carbon arc. Rocket engine sound was simulated by directing a recording of a rocket engine run at an intensity of 122 decibels at the flask. Again no solutions formed but analyses of the individual phases from these and earlier experiments pointed to the direction for future work.

Careful observation disclosed that at least two liquid phases existed even during high speed mixing at reflux temperature. In many cases a third liquid phase was present and in some instances solid phases appeared. The liquid phases were easily distinguished in that they formed layers, the top being pale yellow and the bottome orange. Where a third phase appeared it was seen as a yellow band of liquid between the other two layers. One type of solid phase appeared in the middle layer, another in the lower layer. Using conventional techniques the liquid and solid phases were isolated and submitted for analyses.

It quickly became apparent that the top layers were largely unreacted fuel, the bottom unreacted oxidizer, and the middle reaction products. The crystals in the middle layers were identified as a p-nitrobenzoic acid and those in the bottom layers were oxalic acid. Attempts at further characterization by organic analytical techniques proved futile primarily because of the number of constituents in JP-4. Accordingly, it was decided to rely on experiments with pure hydrocarbons to elucidate the nitration and oxidation reaction sequences obviously in operation. At the same time data from spectrophotometric analyses focused attention on the need for studies under more vigorous conditions and at shorter reaction times.

The spectral approach was to dilute samples of each phase as required with an appropriate solvent, e.g., 2-propanol and measure absorbance as a function of wavelength in the ultraviolet region of the spectrum. A persistent peak occurred at 260 mμ in a curve remarkably similar to ones for nitroaromatics. As indicated earlier, this was quite obvious for mixtures prepared at O/F = 0.3. A plot of all the data at this wavelength for this mixture ratio gave three curves of absorbance vs time corresponding to the top, middle and bottom layers respectively. Extrapolation of these curves back to "0" time showed that significant reaction must have taken place in less than a minute. Extrapolation to "0" time was possible by assigning the absorbance of JP-4 to the upper phase, the absorbance of WFNA to the lower phase, and a value of zero for the middle phase. The fact that absorbances for the middle and lower phases were on the wane beyond the earliest measured time of approximately one minute showed reactions had occurred prior to this point. Subsequent studies explained the decreases in absorgance with time on the basis of interference from products produced by competing oxidation reactions.

The first attempt to reduce reaction time from minutes to milliseconds was made with a crude, manually operated "Y" Tube apparatus. The principle behind such an apparatus is relatively simple. One propellant is flowed at a controlled rate into one arm of the "Y", the other propellant into the second arm. Depending on the flow-rates chosen the propellants mix at a certain mixture ratio and react in the stem. Reaction time is then a function of total flow-rate, cross sectional stem area and effective stem length, i.e., the distance over which reaction is allowed to proceed. The apparatus built to reduce this principle to practice is described as follows.

Two steel tanks fitted with provisions for pressurization were connected to the arms of a metal "Y" Tube having an I.D. of 0.4 cm. In the oxidizer arm was installed an orifice of 1mm and in the fuel arm an orifice of 2mm. Upstream of each orifice was a quick-opening hand valve. Propellants loaded into the tanks and flowed out under 15 psig on the oxidizer side and 20 psig on the fuel side mixed in the stem at an O/F ratio of 0.3 and ejected from the stem at an overall flow-rate of 44 cc/sec. These values were established by flowing methylene chloride (in place of acid) and JP-4 through the system separately to establish mixture ratio and collectively to establish total flow-rate. Methylene chloride has the same density as WFNA and was used during calibrations for safety considerations. The next item has to do with control over effective stem length.

Originally, it was planned to use a "Y" Tube with a transparent stem and monitor reactions by direct spectral analyses at various stations down the stem to provide a record of reaction vs time. Unfortunately, absorbance was too high so a chemical stop was adopted. This consisted of a rapidly stirred, cold solution of equal parts of methylene chloride and n-heptane. Preliminary experiments indicated that such a solution not only quenched reaction but gave the products in form suitable for spectral analysis at a convenient time and location. This approach compounded design problems, though, in demanding a method for isolating a relatively small, representative sample.

This problem was solved by putting a cover with a hole in it on the beaker of quench solution. To the cover was welded a tube with holes overlapping the one in the cover. Into this tube was fitted a second, similarly perforated tube connected to a hydraulic actuator. Steady movement of this tube brought all holes in line momentarily and allowed a definite amount of material to enter the quench solution. Travel was adjusted during runs with methylene chloride and JP-4 to trap 14cc. The balance of the propellant was discarded.

Runs were made with live propellant after the effective stem length was adjusted to 15cm. This is the distance from the intersection of the "Y" to the surface of the quench solution. Under these conditions, reaction time was limited to 43 milliseconds. Following the run, the quench solution was diluted to a given volume and examined spectrophotometrically. Absorbance about 260 mμ was compared with a blank and with that obtained from a composite curve for a corresponding high speed mixing reaction which had been allowed to go to completion. These data showed that about 1/3 as much nitroaromatic forms in 43 milliseconds as in 30 minutes.

Having demonstrated a point, attention was next turned to refining the apparatus for work at higher temperatues and pressures. For safety sake, operation was made remote by replacing the hand valves with a solenoid operated, bi-propellant valve. To increase flexibility, the welded "Y" was replaced with a block drilled to form the channels for the "Y" and tapped to allow insertion of stems of various lengths via standard fittings. To provide better control over flow-rate, vane-type flowmeters were installed. The flowmeters were checked out by flowing a mixture of trichloroethylene and acetone through the system, collecting fractions in given lengths of time and measuring their refractive indices. Mixture ratio was established from a calibration curve and on comparison with flowmeter data showed excellent agreement. To provide better sampling, a shutter-type sampler was built.

The new sampler consisted on a piston-driven shutter programmed to momentarily expose a hole in a perforated, beaker cover. Programming was effected by loading the piston spring to 40 psig with nitrogen gas, then adjusting a bleed valve until 10cc portions of trichloroethylene/acetone mixtures were trapped.

Use of this equipment with two different stem lengths corresponding to 40 and 20 milliseconds of reaction time respectively gave data proving that quench was instantaneous and significant reaction was taking place within 20 milliseconds.

The same results were obtained after installing a back pressure orifice in the stem of the "Y" Tube. This was done in preparation for tests at elevated temperatures. By use of back pressure, reaction in the stem would be restricted to the liquid phase even if the propellants rose above their normal boiling points. Glas-Col heaters were attached to the tanks to allow prerun warm-up.

Satisfactory runs were made in this configuration over the temperature range 75 to 150°F. As anticipated, nitration reactions increased with temperature as shown by an increase in absorbance in the 260 mμ region of the spectrum. Attempts run at temperatures above 150°F were thwarted by a number of problems.

Corrosion of the steel tank by hot acid contaminated the oxidizer with salts and drastically reduced the concentration of the acid. The corrosion problem was solved by using WFNA modified with a corrosion inhibitor. The inhibited acid, called IWFNA, contained approximately 0.5 wgt% hydrofluoric acid.

Uncertainties in temperature due to heat loss in the flow system were solved by installing thermocouples in the arms of the "Y" Tube. The ouput from the fuel arm was fed to a temperature recorder. The ouput from the oxidizer arm was fed to an electronic device wired to activate the sampler on attainment of a predetermined temperature.

Reruns over the temperature range 75 to 150°F gave data equivalent to that obtained with WFNA. No corrosion was encountered above 150°F but thermal decomposition reduced the concentration of the oxidizer. An analysis of the situation showed it took approximately two (2) hours to reach 150°F and during this time water content increased from $< 2\%$ to $> 7\%$ at the expense of nitric acid concentration. Decomposition was reduced by strapping Calrod heaters to the tanks and covering them with insulation. This reduced heating time from hours to minutes. In addition, the tanks were pressurized above the anticipated vapor pressure of the propellant on cessation of heating. With these modifications, a temperature of 200°F was reached with an attendant increase in nitration.

Above 200°F, the flowmeters bound and gave eratic data. The trouble was traced to the Kel-F shaft bearings. Reliability was re-established by replacing the flowmeters with differential pressure gages. These were strain-gage pressure pick-ups installed on either side of the line orifices. Calibration was accomplished by running the differential pressure gages in series with the vane-flowmeters to approximately 200°F.

Attempts to run above 200°F were still unsuccessful though, because of increasing temperature differentials between the tanks and "Y" Tube, and a tendency for the propellants to flash-off on leaving the "Y" Tube. The temperature differential problem was solved by installing the tanks and flow system in an insulated chamber attached to a Chromolox heater. By admitting hot nitrogen to the chamber during the propellant heating cycle and monitoring the operation with a network of strategically placed thermocouples, propellants and hardware were brought to the desired temperature.

The propellant flash-off problem was solved by adding an extension, dubbed a Jet Mixer, to the "Y" Tube stem. This extension, which brought the propellants

outside the insulated chamber, was so designed as to take a stream of cold quench solution from an independent cooling and circulating system and inject it into the issuing propellant stream. The flow-rate of quench solution was determined by prior calibration and the sampler was modified slightly to handle a larger volume of liquid.

In this final form the apparatus was used for runs to 300°F with propellants pressurized up to 575 psig, conditions simulating those of injection into an operating rocket engine. Although there were minor variations, mixture ratio was approximately 0.3 O/F for these runs and reaction time was approximately 20 milliseconds. Again nitration reactions increased with temperature over the entire range studied.

Figure 1 is a schematic for the "Y" Tube apparatus. Figure 2 shows the increase in reaction absorbtion with increase in temperature over the range 75 to 300°F.

Parallel with this work, high speed mixing studies were conducted with pure hydrocarbons of the principal types found in JP-4, viz., paraffins, olefins and aromatics. The compounds chosen were: n-heptane, n-heptene-2 and toluene, all of which contain seven (7) carbons. Through systematic separations, qualitative organic and ultraviolet spectrophotometric analyses, sufficient products were identified to allow postulation of probable reaction sequences. Among the products were acetic acid, oxalic acid, nitroheptene-2, 2-4 dinitrotoluene and p-nitrobenzoic acid.

With heptane, virtually no reaction takes place. (Hence the validity of its use in the quench solution). With heptene, the first reaction is replacement of an olefinic hydrogen with a nitrato group. This is followed by a sequence of oxidation and nitration reactions leading to oxalic acid. Nitration also appears to be the initial reaction with toluene. This occurs in the ring and is followed by oxidation of the chain and further nitration of the ring.

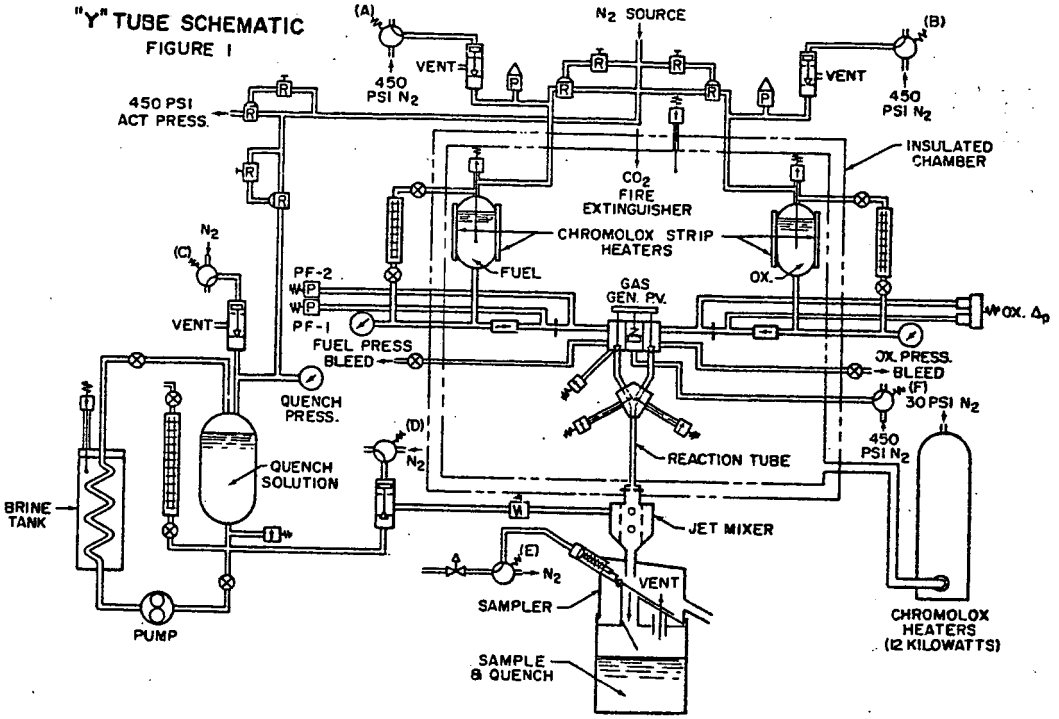
Conclusion

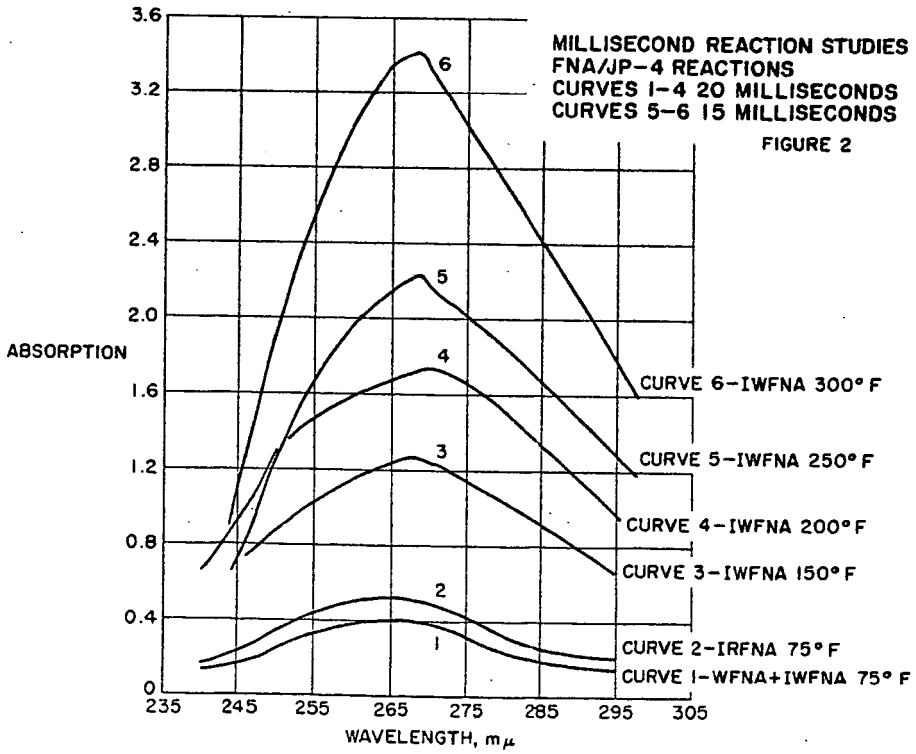
Thus we have shown that liquid phase reactions can occur under rocket engine operating conditions. Further we showed a mechanism for these reactions and indicated how nitration could well get out of hand and lead to combustion instability.

More important we showed the evolution of an apparatus which in its final form is suited for kinetic studies of reactive materials under extreme conditions of temperature and pressure.

But most of all we have demonstrated an approach to a problem which features interaction of the various branches of chemistry and engineering to reach a common goal.

"Y" TUBE SCHEMATIC
FIGURE 1





FLAMMABILITY CHARACTERISTICS OF HYDRAZINE FUELS IN NITROGEN TETROXIDE ATMOSPHERES

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I. INTRODUCTION

The use of hypergolic systems as missile propellants has introduced handling problems not associated with ordinary fuel-oxidant systems. Of particular interest here are the hypergolic systems in which hydrazine fuels are combined with nitrogen tetroxide. The flammability characteristics of such systems have been studied rather extensively at the Bureau of Mines. This report contains the results obtained to date with hydrazine, monomethyl hydrazine, and unsymmetrical dimethyl hydrazine at the Explosives Research Laboratory.

II. EXPERIMENTAL RESULTS

A. NO_2* - Air Mixtures

Minimum spontaneous ignition temperatures (S.I.T.) of liquid hydrazine, unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH), were determined at 25°C. in contact with nitrogen tetroxide (NO_2*)[/]-air mixtures in a modified ASTM autoignition temperature apparatus (1, 2). These tests were conducted by injecting the liquid fuel into a heated atmosphere of NO_2* and air contained in a uniformly heated 250 cc. pyrex erlenmeyer flask. The results of these tests are given in Figure 1 where the S.I.T. is plotted as a function of NO_2* content. In every test the fuel and oxidant reacted on contact producing a white cloud of fine particles; however, as noted in the figure, this reaction did not always culminate in an ignition. Although 70 μliters of liquid fuel was normally used in each test, preliminary studies showed that the S.I.T. was independent of the fuel volume down to at least 10 μliters. Time delays between injection of the liquid and ignition, when it occurred, were imperceptible to the observer. The short horizontal lines appearing on the curves in Figure 1 indicate the uncertainty in the NO_2* concentration (±0.8 volume percent at 100°C.). Approximately 100 separate tests were conducted to establish each curve.

The results of Figure 1 show that at ambient temperature (25°C.) liquid UDMH ignites spontaneously in those NO_2*-air mixtures containing more than about 8 volume percent NO_2*; similarly, MMH and hydrazine ignite in NO_2*-air mixtures containing more than about 11 and 14 percent, respectively. At temperatures above 50°C. the MMH ignites in the presence of lower concentrations of NO_2* than does UDMH.

In the first experiments, the liquid fuel temperature was maintained at 25°C.; however, since higher ambient temperatures are encountered in practice, we determined the effect of liquid temperature on the S.I.T. of the fuels. Figures 2, 3 and 4 show the results of this study. For both liquid hydrazine and UDMH at any fixed concentration of NO_2* in air, the S.I.T. was found to increase with decreasing

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[/] NO_2* represents the equilibrium mixture of NO_2 and N_2O_4.

liquid temperature. This appears to be in agreement with the results predicted by the thermal theory of ignition since an increase in the fuel vapor concentration (due to an increase in the liquid temperature) increases the reaction rate at any specified oxidant temperature and concentration and thereby lowers the S.I.T. However, the corresponding results for liquid MMH at 36°, 55° and 67°C. appear to be anomalous and further study is indicated.

B. NO_2*-O_2-He Mixtures

To determine the effect of thermal conductivity of the oxidizer on the S.I.T. of UDMH, a series of ignition temperature tests was conducted with "air" (HeAir) in which the nitrogen was replaced with helium. The S.I.T. curve obtained under these conditions is given in Figure 5, curve a (upper branch). Comparison of this curve with curve a in Figure 1 shows that the S.I.T. of UDMH in NO_2*-HeAir is the same as that in NO_2*-Air.

The S.I.T. curves obtained in NO_2*-O_2, NO_2*-He and various NO_2*O_2-He mixtures are also given in Figure 5. One can see from these results that very small (0.3%) quantities of oxygen in helium have a substantial effect on lowering the S.I.T. One would therefore suspect that the oxygen acts as a third body in the kinetic mechanisms (3). The addition of further quantities of O_2 has a less pronounced effect on the S.I.T. of UDMH.

C. Effect of Pressure

In an effort to determine the effect of moderate oxidant pressure changes on the S.I.T. of these liquids, a series of experiments was conducted on UDMH in a pyrex-lined steel container at 15 and 45 psi. initial pressure; the container was equipped with suitable hardware for pressure measurement and introduction of the gases and liquids. The results obtained at these pressures are given in Figure 6. The results obtained here at 15 psia. agree with those obtained at atmospheric pressure in the modified ASTM apparatus (Figure 1). Normally the S.I.T. of a fuel is not affected appreciably by moderate changes in pressure. For example, an increase in pressure from 15 to 45 psia. lowers the S.I.T. of UDMH in air by 4°C. (Figure 6). However, as NO_2* is added to the air, the difference between the S.I.T. values at these two pressures increases and then eventually decreases again. Since a small increase in pressure shifts the NO_2* equilibrium towards N_2O_4, we would expect a change in the S.I.T. with changing N_2O_4/NO_2 ratio if the reactivity of the two species (NO_2 and N_2O_4) differ. This is illustrated in Figure 7 where the changes in the ratio $\frac{N_2O_4}{N_2O_4+NO_2}$ and in the NO_2* concentration (ΔNO_2*) for a 30 psi. change in pressure are plotted as a function of the S.I.T. This figure shows a direct correlation between the change in N_2O_4 concentration and the change in NO_2* concentration for the pressure change considered. In other words, for a given NO_2*-air mixture the S.I.T. decreases with increasing pressure because the NO_2* equilibrium shifts towards increasing concentration of the more reactive N_2O_4. If N_2O_4 had been the less reactive specie the S.I.T. would probably have increased initially with increasing pressure.

D. Vaporized Fuel

The above investigations were conducted with liquid fuel; however, similar results can be obtained with gaseous fuel. Such data were obtained for UDMH by vaporizing a measured volume of liquid in air in the modified ASTM apparatus. NO_2* was then injected into this heated mixture to determine if an ignition would result.

Figure 8 shows the results of this study; the S.I.T. is given here as a function of the UDMH concentration in the UDMH-air mixture. From this figure we see that at 25°C. a UDMH-air mixture containing greater than 9 volume percent UDMH will ignite spontaneously on contact with NO_2* at the same temperature.

The lower limit of flammability (L.L.) line of UDMH-air mixtures is included in Figure 8. Mixtures with UDMH concentrations below the L.L. line are considered nonflammable so that we would not expect them to ignite spontaneously on contact with NO_2*. However, there is also a range of mixture compositions between the L.L. line and the S.I.T. curve that are not ignited in this manner; an external ignition source (flame, spark, etc.) would be required to ignite these mixtures.

III. CONCLUSIONS

1. At ambient temperature (25°C.) and pressure, liquid hydrazine, monomethylhydrazine and unsymmetrical dimethylhydrazine ignite spontaneously in NO_2*-air atmospheres containing NO_2* concentrations greater than about 8, 11 and 14 volume percent, respectively. These results appear to be independent of the fuel volume down to at least 10 μliters. An increase in the liquid fuel temperature appears to decrease the NO_2*-air mixture temperature required for spontaneous ignition.

2. The addition of small quantities (0.3%) of oxygen to an He-NO_2* mixture lowers the S.I.T. of UDMH considerably (as much as 50°C.). This indicates that oxygen may be acting as a third body in the kinetic reactions leading to ignition.

3. A moderate increase in pressure tends to decrease the S.I.T. of UDMH in NO_2*-air. The amount of decrease varies with addition of NO_2* to the air in the same manner as the mole fraction of N_2O_4.

4. At ambient temperature and pressure, mixtures of UDMH vapor and air ignite spontaneously on contact with NO_2* provided the UDMH concentration in the UDMH-air mixture exceeds about 9 volume percent.

IV. ACKNOWLEDGMENT

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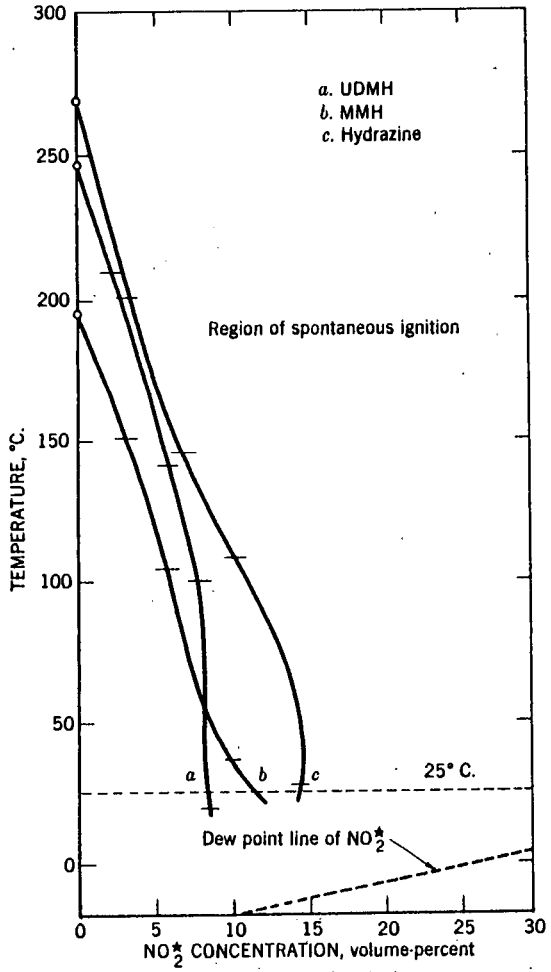

Figure 1.--Minimum spontaneous ignition temperatures of liquid hydrazine, MMH and UDMH at an initial temperature of 25°C. in contact with NO_2*-air mixtures at 740±10 mm. of Hg pressure as a function of NO_2* concentration.

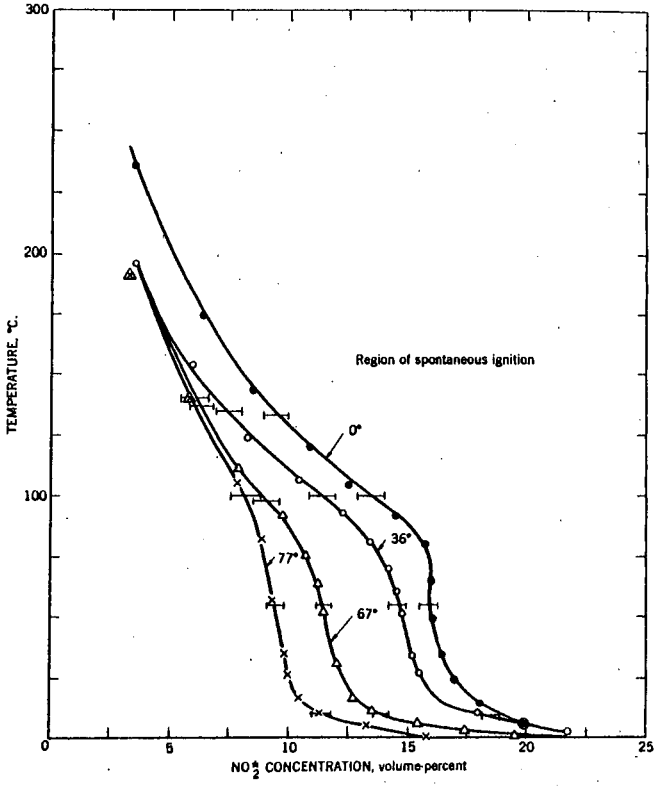

Figure 2.--Minimum spontaneous ignition temperatures of liquid hydrazine at various initial temperatures in NO_2*-air mixtures at 740±10 mm. of Hg pressure as a function of NO_2* concentration.

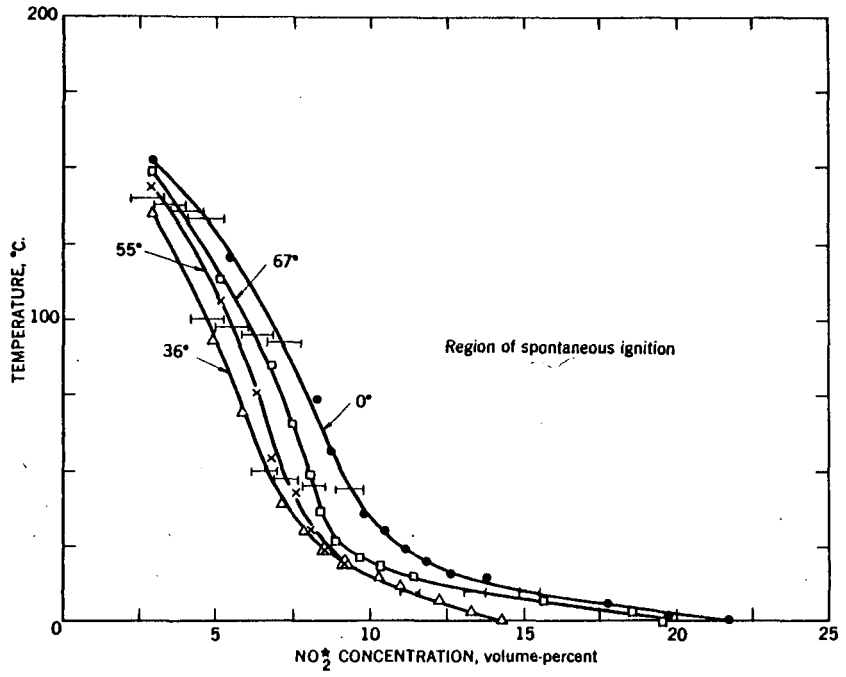

Figure 3.--Minimum spontaneous ignition temperatures of liquid MMH at various initial temperatures in NO_2*-air mixtures at 740±10 mm. of Hg pressure as a function of NO_2* concentration.

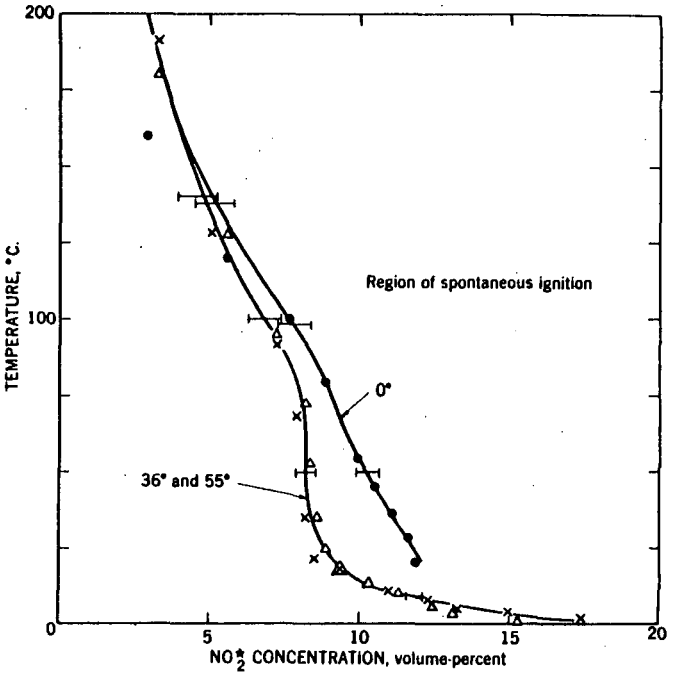

Figure 4.--Minimum spontaneous ignition temperatures of liquid UDMH at various initial temperatures in NO_2*-air mixtures at 740±10 mm. of Hg pressure as a function of NO_2* concentration.

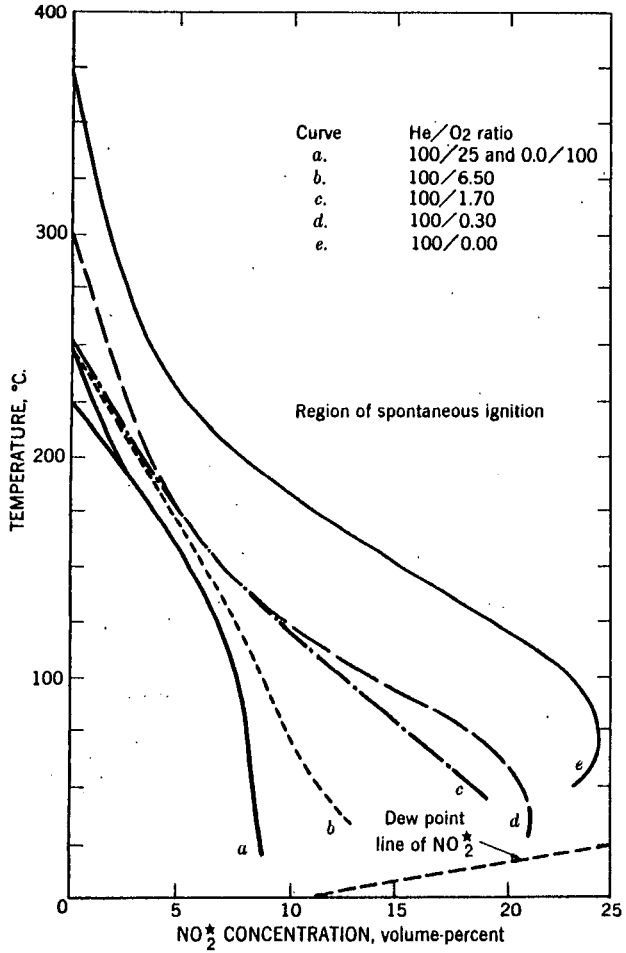

Figure 5.--Minimum spontaneous ignition temperatures of 0.05 cc, of liquid UDMH in $He-O_2-NO_2*$ atmospheres at one atmosphere pressure for various He/O_2 ratios.

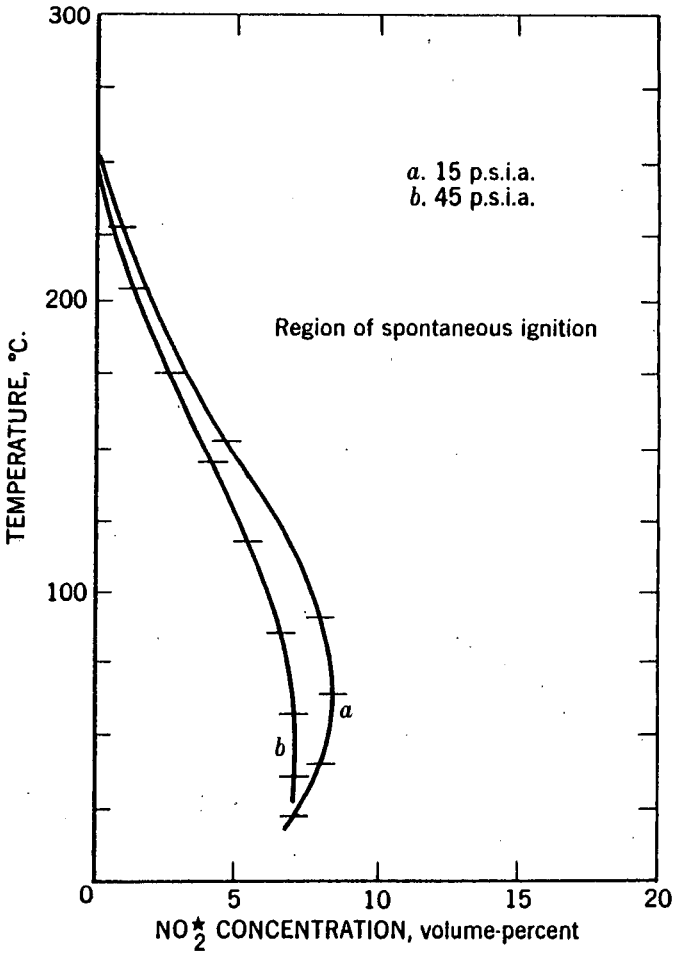

Figure 6.--Minimum spontaneous ignition temperatures of 0.05 cc. of liquid UDMH in NO_2*-air mixtures at 15 and 45 psia. pressure as a function of NO_2* concentration.

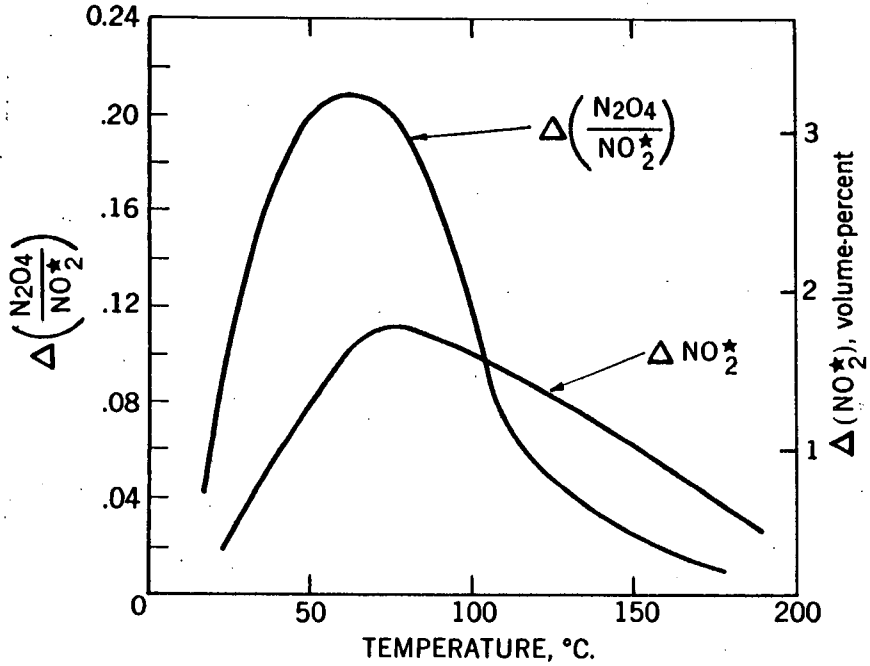

Figure 7.--Effect of temperature on the differences in NO_2* and in the mole fraction of N_2O_4 in NO_2* due to a change in pressure (45 to 15 psia.).

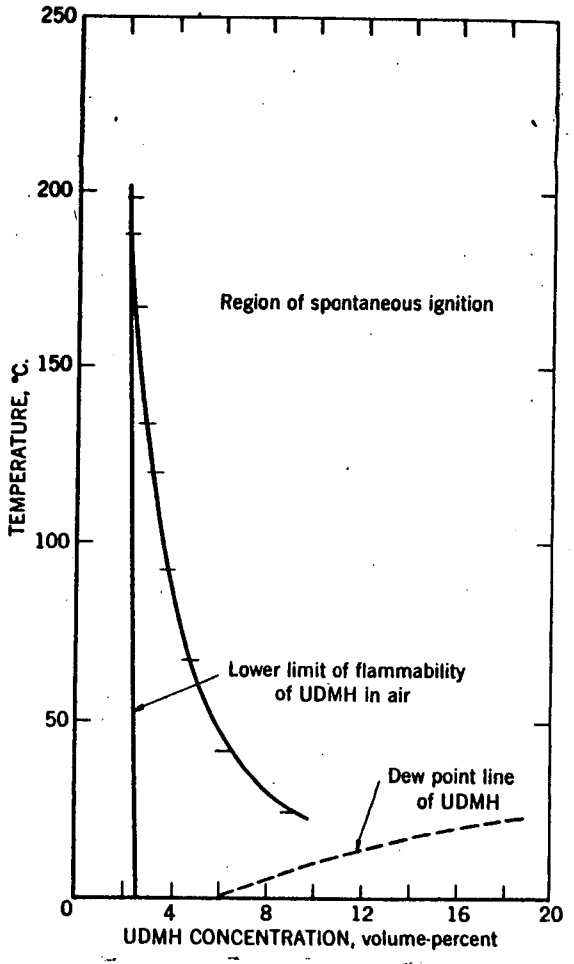

Figure 8.--Minimum spontaneous ignition temperatures of vaporized UDMH-air mixtures in contact with 100% NO_2* at 25°C. and 740±10 mm. of Hg Pressure as a function of UDMH concentration in air.

ABSTRACT

TITLE OF PAPER: The Reactions of Pentaborane-11 With Unsaturated Hydrocarbons

AUTHORS: A. Levy and E. A. Lawton

PLACE WORK WAS DONE: Battelle Memorial Institute
Columbus 1, Ohio

Conditions have been established for reacting pentaborane-11 with olefinic and acetylenic compounds. Depending upon the reaction conditions, gel-like and liquid products are obtained from reactions with olefins, while the acetylenes yield only gel-like products. The liquid products have been examined with respect to physical properties, molecular weight, elemental analysis, methanolysis, mass spectrographic and infrared analysis, thermal stability, pyrophoricity, and heat of combustion. A structure is proposed from this evidence for the new product.